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2/24/2004 Page 1 of 11  
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*Unofficial*

Application No. 09/749988. Formal Amendment

I have just submitted a 137 page fax, sent in two parts, as a formal amendment. During the faxing I noted that two of the replacement drawings seemed to have gone through together and thus may not have faxed properly.

I have attached all 10 of the replacement drawings to ensure that you have received all of them. It is also possible that in such a long fax other pages may have faxed incorrectly. Could you please check for completeness and notify me of any pages which need to be refaxed.

Yours truly,

Stephen M. Lord  
Attachments: Replacement Drawings      Figure 1a-6c

5

### Brief Description of the Drawings

Figure 1a shows the basic way in which the inventions may be combined in a machine for the production of granular silicon.

- 10 Figure 1b shows a plan view of multiple tubes and heaters used in the heating of a larger reactor.

Figure 1c shows a cross section along line A-A of Fig 1b.

Figure 2 shows a more detailed schematic of a preferred method to design a silane fluid bed reactor using dual stage injection of silane.

- 15 Figure 3a shows a more detailed schematic of a preferred method to heat a trichlorosilane fluid bed reactor using a second stage with injection of hot hydrogen gas and TCS and DCS recovery.

Figure 3b is a schematic diagram illustrating one way in which the concepts of the invention for recovery of TCS and DCS can be combined into a complete

- 20 reactor system.

Figure 4a shows a longitudinal cross section, of a water-cooled nozzle.

Figure 4b, an expanded detail of the water flow in Fig 4a.

Figure 4c is an end view of a water-cooled nozzle shown in Fig 4a.

Figure 4d shows the details of the fabrication of the ball joint of the water-cooled

- 25 nozzle shown in Fig 4a.

Figure 4e shows the cross section at line B-B of Fig 4d.

Figure 4f shows the details of the fabrication of the nozzle tip and reactor connection of the water-cooled nozzle shown in Fig 4a.

Figure 4g shows the cross section at line C-C of Fig 4f.

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5 Figure 5 shows a layout of the silicon containing gas heater using heat transfer fluid and alternates of internal and external heating of the fluid.  
Figure 6a shows a schematic of the bead removal and sieving system  
Figure 6b shows an alternative design of the sieving system.  
Figure 6c shows a cross section at line A-A of Fig 6b.

10

### Detailed Description of the Preferred Embodiments

Detailed descriptions of the preferred embodiment are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details disclosed herein are not to be  
15 interpreted as limiting, but rather as a basis for the claims and as a representative basis for teaching one skilled in the art to employ the present invention in virtually any appropriately detailed system, structure or manner. In order to produce high purity silicon suitable for use in semiconductor or photovoltaic applications it is necessary to form and purify a liquid or gaseous  
20 silicon containing material then decompose that material back to solid silicon. Processes to do this have been patented using materials that contain silicon and hydrogen and/or a halogen such as chlorine, bromine or iodine. Such materials include silane, trichlorosilane, dichlorosilane, silicon tetrachloride, tribromosilane etc. It is also common to include a diluent, which may partake in the reaction  
25 such as hydrogen or be inert such as argon. It is most desirable to recover the material in a convenient pellet or granular form and to have a low cost energy efficient conversion process and to convert as much of the feedstock as possible to usable product. Many patents have identified fluid beds as the appropriate technology to accomplish these aims. Implementation of the fluid bed technology  
30 has proved difficult and one of the most difficult problems has been providing

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5 sufficient heat at the inlet of the reactor. The heating problem has led to compromises in other areas notably purity and feedstock conversion.

Lack of heat when using silane leads to hydrogen contamination of the product and a dusty product that is not very usable although most of the silane is  
 10 converted. Lack of heat when using trichlorosilane, or other halogen containing feedstocks, leads to poor feedstock conversion. Attempts to increase the feedstock conversion require higher temperatures and lead to contamination from high temperature materials of construction such as graphite or silicon carbide, operating with low feedstock conversion leads to increased cost in  
 15 feedstock production and byproduct disposal or use of more expensive production methods which use higher pressures and temperatures to recycle the byproducts.

Another major problem has been sintering of the granules either at the reactor  
 20 entry or in the body of the bed of particles. Methods of dealing with this problem have been cooling the beads at the entry, using low concentrations of the silicon depositing gas and operating with very vigorous fluidization. Cooling the beads at the entry exacerbates the inlet-heating problem discussed above as does operating with vigorous fluidization. Using low concentrations of the silicon  
 25 depositing gas leads to the uses of large amounts of inerts and the consequent problems of the higher capital and operating cost required to recycle, heat and purify the inerts, which must be maintained exceptionally pure.

A further related problem has been controlling the particle size of the granules in  
 30 the reactor. It is desired to produce beads that are large and of a narrow size  
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- 5 distribution but the reactor fluidizes better with a wide size range and it is desired to minimize contamination in the production of seed. Previous methods of dealing have some or all of the following techniques; particle separation and grinding of seed particles and reintroduction of the seed to the reactor and have done them either internally or externally to the reactor. The problem with
- 10 external techniques has been the contamination and difficulty of control since there is a long lag time (1-2 days) between introduction of small seed particles and their growth to product size. Internal techniques have suffered from the difficulty of separating large granules out and of generating sufficient seed.
- 15 This proposed machine for production of granular silicon incorporates several novel features into its design in order to overcome the above problems without the compromises inherent in the prior technology. The main novel features are; separating the heating of the silicon feedstock gases from the non silicon containing gases and heating the latter to a temperature above the reactor
- 20 temperature; heating the granules in a heater section and using the pulsing of the gas flow to move the beads into and out of a reactor section; cooling only the localized area around the silicon feedstock entry and minimizing said entries; providing non-contaminating sieving and grinding techniques for online removal
- 25 feedstock recovery subsystem which can recycle the byproducts to extinction and providing multiple heater/reactor stages in one vessel.

Additional novel features are; heat recovery from granules by direct contact with non silicon containing gases; external flow control of each injection point; heating

30 of the silicon containing gases by a liquid or vapor whose temperature is not high

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5 enough to cause decomposition of the gases, measuring reactor weight and pulsing force continuously and using one or more high efficiency cyclones to removes small diameter dust.

Additional benefits of the design are that separating the heater and reactor  
10 section enables the use of cheap resistance heaters and of different diameters for the two sections, the pulsing action itself polishes the granules, recirculation and reinjection into the reactor of the undersize granules provides new seed particles.

15 In accordance with the present invention, Figure 1a shows a basic version of the invention incorporating several of the novel features in an integrated design that is suitable for production of granular silicon from any silicon containing gas (e.g. silane, dichlorosilane, tribromosilane or trichlorosilane). The recycle of solids is done using a pulsing technique where most of the hot granules in the heater  
20 zone are pushed up into the entry of the reactor by a pulse of gas into the bottom of the heater, Stream 5. At the end of the pulse, colder solids fall down by gravity into the heater for heating and recycle upwards during the next pulse. The pulsing of the beads and gas also provides additional agitation of the bed compared to the agitation provided by the equivalent continuous flow. Such  
25 agitation is particularly useful for silane-based systems, which are primarily limited by the related operational problems of agglomeration and plugging and have been limited to low silane concentrations in the feedstock. Thus the additional heat and agitation provided by pulsing can be used to increase the silicon feedstock flow, stream 1, and thus increase the silicon production, Stream

30 15. In Fig1a, stream 1 is shown as broken into two streams each of which have

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5 their own pulsing devices and inlet coolers, 8a and 8b, which are cooled by inlet water flows 9a and 9b and drained by outlet water flows 10a and 10b.

Additional streams typically provided for use in purging lines, initial fluidization, wall deposit etching and shutdown are not shown but are required as is usual for such reactors. Such streams include argon and/or nitrogen for purging and

10 fluidization during startup and shutdown and an etching gas such as chlorine or hydrogen chloride for wall deposit etching at the end of the run prior to shutdown.

The reactor is supported on a weigh cell or cells, 17, which can provide continuous information on the weight of the reactor and bed and the force of the\* pulses. Since the pulses are regular and at a known frequency this information

15 can be separated from the longer term weight changes by standard frequency analysis techniques. In order to provide accurate information the lines

connecting to the reactor must be flexible enough to avoid interfering with the displacement of the weigh cell. Such flexibility is also required to prevent damage to the quartz reactor and allow for differential thermal expansion. This flexibility

20 requirement is one reason for the use of the water-cooled ball joint connections with elastomeric O-rings for the nozzle connections, which are shown in Fig 4a-g.

An example of silicon deposition using the design similar to that shown in Figure 1a but with three silane inlets, three pulsing devices and three inlet coolers, three water inlets, and water outlets instead of the two inlets shown in Fig1a is as

25 follows:

A quartz vessel consisting of a bead and gas heater zone of 90 cm length and 5 cm in diameter and an insulated reaction zone of 600 cm length and 10 cm diameter was loaded with a 240 cm bed of 850 micron average diameter silicon beads. The three silane inlets for stream 1 were located 100 cm above the

30 bottom of the vessel. The reactor, effluent piping and cyclone are well insulated.

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5 The reactor was brought up to 750-800°C using argon as a heating and fluidizing gas through stream, 5, with a small purge stream flow through stream 1. Most of the argon was recycled through stream 5 with some being vented to the effluent gas stream, 4. The hydrogen preheater and the bead /gas heater were set at 900°C, the SCG vapor temperature heater was set at 350°C. The upper wall

10 heaters were set at 850°C. The pulsing of the argon flow on streams 1, 2 and 5 was started at 0.25 cycle per second in phase. A small cooling water flow of 20 ml/min for each cooling water streams 9a,b&c, 9c not shown in Fig 1a, was started to the silane inlet cooling devices 8a, 8b, 8c, 8c not shown in Fig 1a, to provide thermal isolation of the inlet from the reactor temperature. The inlet water

15 temperature was 35°C and the outlet temperature of the exit cooling water streams, 10 a, b&c, 10c not shown in Fig 1a, was 57°C for a parasitic heat loss of 90 watts. A small flow, 1SLM, of argon was started through stream 2 to the bead cooler, 12 and a flow of 1 SLM of argon was started to the granule recycle line 16 and silicon sieve, 14, through stream 3. A small flow of water (100 ml/min)

20 was started to the bead cooler, 12, through stream 11 and exited via stream 13. Then high purity (less than 2 ppmwt carbon oxides and less than 2ppmw methane) hydrogen was bled into all four streams 1,2,3&5 to displace the argon with the recycle, 5, partially closed and effluent gas stream 4 opened more.

Once the reactor was at temperature and operating on hydrogen, the

25 temperature of the vapor in the silane heater for stream 1 was controlled at 350°C and silane was slowly introduced. Pulsing continued at 0.25 cycles per second. Simultaneously the temperature of the hydrogen/bead heater at the bottom of the reactor was increased to design conditions of 1000°C for the heater temperature. At stable operating conditions the silane flow, 1, and the recycle

30 hydrogen flow, 5, varied between 30-300 SLM to provide the pulsing and were in

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5 phase with each other. The three individual silane flows each varied between  
10-100 SLM in phase. Average bed temperature was 860°C at the bottom,  
dropping to 840°C at the top of the bed and 685 C at the top of the reactor.  
Recycle gas from the cyclone was at 410°C and from the hydrogen recovery unit  
was 100 °C. The bed was observed to be slugging vigorously at the pulsing  
10 cycle of 0.25 cycle/sec and some dust was carried over into the cyclone but  
pressure drop was stable during the run.

Beads were removed by adjusting the hydrogen flow and pulsing cycle of stream  
2. As a pulse of beads left the bead cooler, 12, and went into the silicon sieve,  
15 14, beads from the reactor fell into the bead cooler, 12. The beads going in to  
the silicon sieve, 14, spread out and either fell through the sieve or were retained  
and exited as the product stream, 15. The beads falling through the sieve were  
moved by the pulsing of stream 3 back into the reactor via the granule return line,  
16. The pulsing of stream 3 also assisted in preventing blinding of the sieve, 14.  
20 Initially most of the beads were smaller than the sieve opening of 1.2 mm and so  
were recycled. At stable operation the bead removal rate of stream 15 was 13.5  
Kg/hr and the bead exit temperature was 80 C. As the bead removal rate was  
increased the flow of hydrogen through stream 2 was increased and the flow  
through the hydrogen preheater was decreased while maintaining the total flow  
25 of 30-300 SLM. The flow of stream 3 varied between 10-100 SLM. Thin wall  
deposits were formed but could be etched off easily at the end of the run. After  
the run the mass balance showed the deposited silicon was about 95% of the  
theoretical yield and no major agglomerates were seen. Power to the  
hydrogen/bead heater was 3 kW on average. Power to the silane heater was 3  
30 kW on average. Power to the hydrogen preheater was 5kW initially decreasing to  
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5 3 kW as the hydrogen flow to the preheater was reduced by the increase in flow to the bead cooler, 12. Power to the upper wall heaters varied between 3 and 5 kW depending on the amount of cold undersize granules recycled to the reactor. Total power was 12 to 16 kW for a production rate of 13.5 kg/hr, which is about 1kW/kg. Energy requirements are based on a silane vapor feed.

10

Scale up of these reactors is much more feasible than in previous technology as is illustrated in Figs 1b & c. The diameter of the main reactor is increased from 10 cm to 50 cm which means increasing the cross-sectional area, throughput and heat input requirements by 25 times. The bead heaters need to deliver 25 times more heat and so must increase in surface area and /or in the temperature of the heater.

In the example, shown in figs 1b & c, a center tube, 20, is increased to 10 cm thus doubling the surface area per foot and an additional 8 tubes, 24a-g, each 10 cm in diameter are provided in an outer ring. This provides 17 times the surface area per foot and the length of the heaters is increased by 50% thus providing 25 times the surface area. Alternatively the length could be increased by 30% and the temperature difference from the heater to the tube increased by 20% from 50 deg C to 60 deg C to provide the additional heat transfer. Thus there are three parameters that may be adjusted to provide the extra heat transfer, the surface area/ft, the length and the temperature difference. In practice a higher temperature difference shifts the frequency of the radiant heat towards the visible and more is transmitted through the quartz, which is an additional benefit. It is also necessary to increase the number of silicon containing gas inlets and here it is shown that 8 inlets, 8a-g, are provided for the 25-fold increase in flow.

30

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5 Increasing the inlet diameter and/or the pressure drop across them can do this.

The fraction of heat input lost to parasitic heat loss from cooling the nozzles decreases by a factor of three.

In this design the heater elements are arranged in two rings an inner ring 22, and an outer ring 23. This provides an efficient furnace. The outer ring is insulated,

10 23, on the outside, top and bottom. The top of the inner ring heater may or may not be insulated depending on the distance of the heater from the silane inlet nozzle. In general for larger reactors it is not insulated, as shown, to provide more heat and in smaller reactors it is insulated to reduce the wall deposits. Gas flow to each tube is pulsed and this may be done in any convenient fashion

15 providing that the flow is evenly distributed. Since it is convenient for bead removal to be done via the center tube, this tube will normally have its own flow controller.

An example of silicon deposition using a dual stage reactor that is  
20 designed for silane and is similar to the design shown in Figure 2 but with six silane inlets, each with an associated pulsing device, inlet cooler, water inlet and water outlet, instead of the four inlets shown in Fig. 2 is as follows.

A quartz vessel consisting of a lower bead and gas heater zone of 90 cm length and 5 cm in diameter and a lower insulated reaction zone of 150 cm length and  
25 10 cm diameter and an upper bead and gas heater zone of 90 cm length and 10 cm in diameter and a upper insulated reaction zone of 570 cm length and 13 cm diameter was loaded with a 480 cm bed of 850 micron average diameter silicon beads. The reactor, effluent piping and cyclone are well insulated. The hydrogen<sup>®</sup> preheater and the bead /gas heater were set at 900 °C, the SCG heater vapor  
30 temperature was set at 350 °C. The lower wall heaters were set at 950 °C and

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5 the upper wall heaters were set at 850 °C. The pulsing of the argon flow on streams 1, 2 and 5 was started at 0.25 cycle per second in phase. A small cooling water flow of 20 ml/min each was started through cooling water inlet lines, 9a,b&c, 9c not shown in Fig 1a, and 19 a, b&c, 19c not shown in Fig 2a to the silane inlet cooling devices 8a, 8b, 8c, 8c not shown in Fig 2a and 18a,b &c, 18c not shown in Fig 2a to provide thermal isolation of the inlet from the reactor temperature. The inlet water temperature was 35 °C and the outlet temperature was 57 °C at the cooling water exit lines, 10 a,b&c, 10c not shown in Fig 2a and 20 a, b&c, 20c not shown in Fig 1a for a total parasitic heat loss of 180 watts. Other conditions and start up procedures were done as for the example above.

15 At stable operating conditions the silane flow, 1, varied between 60-600 SLM and the recycle hydrogen flow, 5, varied between 30-300 SLM to provide the pulsing and were in phase with each other. The six individual silane flows each varied between 10-100 SLM in phase. Average bed temperature was 860 C at the bottom, dropping to 840 °C at the top of the bed and 665 °C at the top of the reactor. Recycle gas from the cyclone was at 400 °C and from the hydrogen recovery unit was 100 °C. The bed was observed to be slugging vigorously at the pulsing cycle of 0.25 cycle/sec and some dust was carried over into the cyclone but pressure drop was stable during the run.

25 Beads were removed as in the example above. The flow of stream 3 varied between 20-200 SLM. The wall deposits that were formed were thicker than in the first example but still could be etched off easily at the end of the run. After the run the mass balance showed the deposited silicon was about 95% of the theoretical yield and no major agglomerates were seen. Power to the hydrogen/bead heater was 3 kW on average. Power to the hydrogen preheater

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5 was 5kW initially decreasing to 1 kW as the hydrogen flow to the preheater was reduced by the increase in flow to the bead cooler. Power to the silane heater was 6 kW on average. Power to the lower wall heaters was 3kW on average. Power to the upper wall heaters varied between 5 and 7 kW depending on the amount of cold undersize granules recycled to the reactor. Total power was 22  
10 to 24 kW for a production rate of 27 kg/hr, which is about 0.8-0.9 kW/kg. While not shown it is also possible to provide a recycle bead heater on stream 16 which will reduce the load on the upper wall heater and thus tend to reduce wall deposits in that area.

15 An example of silicon deposition using dual stages and designed for trichlorosilane using a design similar to that shown in Figure 3a but with 3 Trichlorosilane inlets, and 3 hydrogen inlets, and associated pulsing devices and inlet coolers, water inlets, and water outlets, instead of the 2 trichlorosilane and 2 hydrogen inlets shown in Fig. 3a is as follows:

20 The same quartz vessel and silicon granule bed as used in Example 2 is used. A hydrogen superheater is supplied capable of heating hydrogen to 1300 °C using Kanthal heating elements. The important function of increasing the yield of silicon from trichlorosilane is shown using gas heating in conjunction with wall heating.

In the trichlorosilane decomposition there are two main reactions; thermal  
25 decomposition to silicon and silicon tetrachloride and hydrogen reduction to silicon and hydrogen chloride. The second reaction produces more silicon per mole of trichlorosilane but requires dilution with hydrogen and higher temperatures. Since the reactions are equilibrium reactions the products of the reaction of the reaction inhibit the reaction so direct recycle of effluent is not

30 advisable. Instead the residual hydrogen must be extracted from the effluent and

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5 recycled through an external hydrogen recovery system and some additional  
hydrogen is required. In this reactor the lower stage operates at lower hydrogen  
to TCS ratio and at a lower temperature so the thermal decomposition reaction is  
more important. In the upper stage the hydrogen to TCS ratio and the  
temperature is increased thus using the hydrogen reduction reaction to obtain  
10 additional yield of silicon. Since the TCS is fed as a liquid some changes were  
made to the metering equipment and to the preheater which now also was to be  
used as a vaporizer. The heat requirement were a little less than for silane  
because of the lower TCS flow. In order to maintain the pulsing, spray nozzles  
and liquid solenoid valves were placed directly on the inlet to the vaporizer.

15

A small cooling water flow of 60 ml/min was started to the silane inlet cooling  
devices 8a, 8b, 8c, 8c not shown in Fig 3a, (20 ml ea) and 90 ml/min to 18a, b  
&c, 18c not shown in Fig 3a, (30 ml ea) to provide thermal isolation of the inlet  
from the reactor temperature. The inlet water temperature was 35°C and the  
20 outlet temperature was 57°C for 8a, b &c and 65°C for 18,a,b &c for a parasitic  
heat loss of 270 watts. . Other conditions and start up procedures were done as  
for the example above. After startup on hydrogen was achieved with the bed at  
850°C the temperatures of the hydrogen/bead heater at the bottom of the reactor  
was increased to 1000°C, the lower wall heaters were increased to 1050°C and  
25 the upper heaters to 1150°C.

At stable operating conditions the trichlorosilane/dichlorosilane (98% TCS) flow in  
stream 1 was 12-120 SLM (4-40SLM per injector) and the temperature was  
350°C, the ultra pure (less than 0.2 ppmwt carbon oxides and 0.2 ppmwt  
30 methane) hydrogen flows in stream 5 and 17 were varied between 30-300 SLM  
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5 thicker in the wall heater zones but still could be etched off easily at the end of the run. After the run the mass balance showed the deposited silicon was about 95% of the theoretical yield and no major agglomerates were seen. Power to the hydrogen/bead heater was 4 kW on average. Power to the trichlorosilane vaporizer/heater was 2.5 kW on average. Power to the hydrogen preheater was 10 5kW, to the hydrogen superheater was 10 kW. Power to the lower wall heaters was 3kW on average. Power to the upper wall heaters varied between 5 and 7 kW depending on the amount of cold undersize granules recycled to the reactor. The silicon production was 1 kg/hr, which is about 25% of the silicon in the TCS. Power required was about 30 kW/kg. Energy requirements are based on a 15 trichlorosilane liquid feed. It should be noted that in a dedicated TCS reactor the upper injectors for superheated hydrogen only need to be cooled at the joint not at the reactor penetration, which would save a small amount of heat (about 150 watts). The energy required to vaporize and heat the silicon tetrachloride is not included because this is part of the recovery operation. Ultra pure hydrogen is 20 required because of the greater hydrogen to silicon ratio in this reactor compared to a silane reactor. The specific level of purity required for the hydrogen diluent may be calculated by mass balance based on the silicon specification and the assumption that all carbon entering the reactor leaves in the silicon product.

25

The benefit of injecting the silicon tetrachloride at the top of the reactor is to move the equilibrium conditions so as to recover additional feedstock. The schematic of this sub-system is shown in Fig 3b. The silicon feedstock stream, 301, is mixed with the recycle stream 317 to form reactor feed stream, 1 which is 30 heated in the TCS heater, 322, to a temperature below its thermal decomposition

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5 temperature. The hydrogen feedstock stream, 302, is mixed with the recycle stream 313 to form reactor feed stream, 5 heated in the hydrogen heater, 323, and then reacts in the reactor, 303. The use of multiple heaters and injection points as done in the preferred embodiment of the reactor does not affect the basic schematic. The silicon product leaves the reactor as Stream 15. The

10 stream 305 enters the recovery reactor 306 (corresponding to the effluent piping and cyclone of Fig3a) where it is preferably combined with the STC stream 21 and cools and reacts to reform the desired feedstock. This stream, 307, exits the recovery reactor and enters the rapid quencher, 308, where the gases are cooled rapidly to prevent decomposition of the newly reformed feedstock. The stabilized

15 gases, 309, exiting the quench are then cooled further in the gas-liquid separator, 310, to condense most of the silicon containing species and the condensed liquids, 311, are separated from the uncondensed gases, 310, which are primarily hydrogen and hydrogen halides and are further treated in a gas separator, 312, to provide a stream, 313, that is primarily hydrogen and a stream,

20 314, that contains most of the hydrogen halide. This gas separator can be a cryogenic device, an absorption or adsorption device, a membrane device or any combination thereof. The liquid stream, 315, is then processed in a liquid separator, 316, into a stream, 317, which is primarily silicon hydrogen halides and a stream, 318, which is substantially free of silicon hydrogen halides. All or

25 part of stream 318 may be recycled to the recovery reactor, 306, through STC heater, 324, as stream 21 or sent directly to the decomposition reactor, 303, through STC heater 325 as in the prior art. As discussed earlier returning the STC stream directly to the decomposition reactor has significant disadvantages which why it is not the preferred option. The separator, 316, will typically be a

30 distillation column but any techniques are suitable which will provide good

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5 separation. The required degree of separation is determined by economics but typically the purity of each stream would be about 98-99%. The benefit of such a scheme is that the effluent from the system is only stream 314 which contains mostly hydrogen chloride which can be directly recycled to react with silicon to make more TCS at >90% yield. There is no recycle of pure silicon containing materials back to the low purity TCS manufacturing unit and there is no waste  
10 STC stream that must be converted to low value silica. Thus while the preferred reactor subsystem is more expensive to build and operate than one without feedstock recovery and thus designed with lower hydrogen flows and higher TCS flows the overall system is more economic because of reduction in costs of the remaining systems. A further reason for this preferred design is that it can easily  
15 be substituted for the standard existing rod reactors because they also recycle the STC to extinction. Use of apparently cheaper reactors which do not fully convert the silicon content in the TCS as substitutes for existing rod reactors would mean either a reduction in silicon output or the need for expansion and  
20 modification of the TCS production and purification facilities.

A key feature of the machine is the localized cooling of the silicon containing gas injector nozzles. Figs 4a-g shows one way this may be implemented. Fig 4a is a cross section of the nozzle assembly. The silicon containing gas at about  
25 350°C, stream 401, comes in through the ball joint, 402, which is sealed by an elastomeric o-ring, 403, positioned in an o-ring groove, 404, and which is cooled by water flowing through a micro-channel, 405, directly under the o-ring groove. It proceeds through the inside of the inner quartz tube 406, which tapers down as  
30 it enters the reactor, 407. The tip of the nozzle, 416, is cooled by water flowing through the circumferential micro-channel, 408 which is cut into the outer wall of  
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5 the inner tube, 406 and sealed against the inner wall of the outer tube, 409.  
 Water flows from the water inlet 410, to the ball joint micro-channel, 405, via a  
 micro-channel, 411, which is cut into the outside of the inner tube 403 and then  
 goes to the tip micro-channel, 408, via a micro-channel, 412 on the other side of  
 the outside of the inner tube 406. This water is returned to the outlet, 414, via a  
 10 return micro-channel 413. There several features which are important. The  
 machining of the circumferential micro-channels must ensure that the water flows  
 evenly on both sides. The water in the circumferential micro-channels must flow  
 fast enough, 10-100 cm/s, to obtain good heat transfer at the tip. The supply and  
 return micro-channels must not cross each other. In Fig 4a the incoming cold  
 15 water goes first to the ball joint via 411 then to the tip via 412 and is returned via  
 413 which is separated from 411 by an uncut section of quartz between the inlet  
 and outlet water tubes, 410 and 414. Fig 4b is an enlarged drawing of the section  
 between the inlet and outlet water tubes, 410 and 414 to better show the water  
 flowpath. Fig 4c shows an end view of the nozzle and illustrates how the inlet  
 20 tube 410 may be bent away from exit tube 414 to provide access for connections.  
 This design provides higher flow rates than if the flow was divided and avoids the  
 problems of starving one section through flow maldistribution.

It is of course possible to have more than one circumferential micro-channel  
 providing good engineering practice is followed in design and fabrication to  
 25 prevent flow maldistribution. Figs 4d-g show some details of the nozzle tip and  
 ball joint. In Fig 4g the nozzle tip micro-channel, 408, is shown as a micro-  
 channel that is 3mm wide and 0.2 mm deep with its far end 1 mm from the end of  
 the nozzle. The nozzle tip 416 is rounded which reduces chipping damage and  
 removes a hot spot on the end of the nozzle where deposition might occur. The  
 30 nozzle is supported by 4 quartz nibs, 415, which provide additional strength

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5 without contributing much to the heat transmitted back to the nozzle from the  
 reactor wall. In the Fig 4f, which is a cross section A-A, the four quartz nibs, 415,  
 are shown to have little area in contact with the nozzle and the circumferential  
 water channel, 408 is shown as an annular space. In Fig 4e which is the cross  
 section B-B the supply, 412, and return, 413, micro-channels are shown as  
 10 sectors produced by grinding flats on the outer wall of the inner tube 406. It is  
 of course possible to grind multiple flats or to grind other shapes providing that  
 the strength of the inner tube is adequate after grinding and that the hydraulic  
 diameter of the micro-channel is large enough to allow the required cooling water  
 flow at the available pressure drop. In the Fig 4d the ball joint is shown as a  
 15 standard 18/7 ball o-ring joint with a diameter of 18 mm at the widest end of the  
 o-ring groove, 404, a tube outside diameter of 9.5 mm and a nominal internal  
 diameter of 7 mm, sealed to the inside of this is a 5-7.25 quartz tube which has  
 been OD ground to fit tightly. The tight fit provides the water seal between the  
 entrance and return water lines. Circumferential micro-channels are cut in the  
 20 outside of this inner tube to provide the cooling at the ball joint and tip and flats  
 are ground to provide the water connections. The inner and outer tubes are  
 assembled, welded, annealed, ground to obtain the final shape then acid treated  
 to improve the surface finish and strength. The water connections shown are  
 standard 12/2 ball o-ring joint with a diameter of 12 mm at the widest end of the  
 25 o-ring groove, a tube outside diameter of 6 mm and a nominal internal diameter  
 of 2 mm. The relatively thick wall, 2mm, is beneficial in preventing accidental  
 breakage. The problem of accidental breakage is a major design issue for these  
 quartz injectors because of the safety issues involved in handling pyrophoric  
 materials. Simply making the injectors very large with thick walls increases the  
 30 heat transmission back from the reactor and even such designs are prone to

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5 breakage if sufficient force is applied particularly if there is a lever action involved  
 such as is the case with the injectors since they must penetrate the insulation.  
 Thus it is important to prevent movement of the nozzle so the rigid insulation  
 used has recesses cut in the top to support the water connections. It is also  
 important to prevent force being applied to the end of the nozzle by the  
 10 connections so they must be very flexible. The water connections can be small  
 diameter 1/8 inch tubing and coiled helically to provide flexibility. The silicon  
 containing gas connections typically need to be 1/4" tubing, stainless steel and  
 insulated. However the pressure is low so thin wall corrugated tubing can be  
 used and a similar helical coil may be employed. It is also possible to put short  
 15 1 ft. lengths of smaller 1/8in or 3/16 in dia. tubing without increasing the pressure  
 drop too much. The insulation must not restrict the movement of the tubing  
 needed to accommodate differential thermal expansion during the various reactor  
 operations. Selection of the O-ring material is also important as this provides a  
 safety and contamination barrier for the reactor. The o-rings are usually selected  
 20 from an elastomeric fluorocarbon material such as Viton or Kalrez because of  
 temperature considerations. The permeability of such material to contaminants  
 such as oxygen, carbon dioxide and water vapor in the atmosphere varies with  
 material composition and temperature. The materials can also slowly deteriorate  
 giving off contaminants. The most critical consideration is control of the o-ring  
 25 temperature, which should be maintained in the 25-150°C range and preferably  
 around 50°C. It is of course possible to use multiple o-rings for additional  
 protection at some increased expense but all o-rings must have their temperature  
 maintained in the desired temperature range.

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5 Fig 5 shows a layout of a preheater for a silicon containing gas. It consists of a gastight vessel, 501, which contains three helical coils, 502, 503 & 504, of tubing each of the same length coiled concentrically in the top half and one or more electrical elements, 505, in the bottom half. The vessel is filled with high temperature heat transfer fluid, 506, so as to cover the heating element/s, 5, during operation. A temperature indicator controller or TIC, 507, is provided to control the temperature of the fluid below the silicon containing gas decomposition temperature, 300-400°C. Each coil has separate inlets, 508, 509, 510 and outlets, 511, 512, 513. The lid, 514, is flanged to the top of the vessel and is removable for access to the coils. A connection, 517, for a pressure gage and pressure relief valve is provided. The penetrations of the coils through the lid are gas tight, typically welded. During operation the silicon containing gas comes in through the separate inlets and leaves without mixing through the outlets. The coils are free to expand and thus exert no force on the connections through the lid which reduces the risk of leaks commonly found at the tube to tubeplate connection of shell and tube heat exchangers. The heat to the coils is supplied by condensing heat transfer fluid vapor, which is produced by boiling the fluid with the electric heating element, 505. Alternatively the liquid may be removed through liquid outlet, 515, and vaporized in an external vaporizer, not shown as dotted lines, then returned through the fluid inlet, 516, or the liquid may be removed then heated but not vaporized and returned through 516. In this latter case it may be necessary to provide baffles and a higher mass flow rate to provide adequate heat transfer. There are many other variants, such as providing more than three coils, using U-shaped tubes or pancake coils which one knowledgeable in the art can design. The coils may be straight tubing, corrugated, twisted or finned.

In an example of operation of this device the gas tight vessel, 501, was 10 inches in diameter and 15 inches tall and fabricated from 304L stainless steel. It was insulated on the top, bottom and sides with a 2" thick layer of Microtherm G

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5 pressed silica insulation, 518. The coils, 502, 503 & 504 were each 10 ft long and made from 1/4-inch 304L S. S. tubing. The coil diameters were approximately 6 inches, 7 inches and eight inches. The electrical heater was a 4" diameter flange mounted heater of 4 kW with multiple Incoloy sheathed elements. The heat transfer fluid was filled to a depth of 8 inches. The fluid used was Dowtherm A.

10 Temperature of operation was controlled at 360 C (680 F) using the temperature indicator controller. Pressure in the vessel was 75 psig. The three coils each heated an average of 67 SLM of silane each from 20C to 330 C. Actual flow of silane per tube pulsed from 10-100 SLM.

15 Fig 6a. shows a schematic representation of the non-contaminating sieving device. The hot beads, stream 601, fall into a cooler, 602, where a gas stream 603 may cool them, which then goes back up into the reactor thus recovering some heat from the beads. In addition the beads may be cooled by a water jacket, 605, with inlet and outlet streams, 605a & 605b. A gas stream, 606, is  
 20 pulsed into tube, 607, which also may be cooled by a water jacket, 608, if desired. The pulsing gas stream pushes a fixed amount of beads out of the cooler, 602, into the sieve tube 609. The beads fall onto the first sieve, 610, and the beads smaller than the sieve pass through while the larger beads are retained and exit through stream, 611. These beads may be pulsed using the gas  
 25 stream 612 through a tube 613 into a container 614. It is advantageous to use a bead detection device, 615, to adjust the bead flow into the container 614 so as to maintain the exit tube, 611, full or nearly full of large beads. This reduces the chance of smaller beads exiting with the large beads and provides a measurement of the flow of large beads since the pulsing flow of the gas stream,  
 30 612, may be correlated with the bead flow. The sieving process may be

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5 repeated as shown with a smaller size sieve, 616, using tubes 617 and 619, gas  
flow 618 and container 620. The residual undersize beads then fall to the bottom,  
621, where they can be removed via tube 623 and gas stream 622 to a  
container, 624. This container can be used to replenish the reactor in a variety of  
ways apparent to one skilled in the art including pneumatic transport and  
10 physically moving the container to a bead feeding port. Such beads may also be  
reheated. All material with which the beads come into contact must be  
noncontaminating. Such materials include electronic grade silicon and high purity  
silicon oxide. The degree of contamination that may be permitted is higher for the  
product beads than for the return beads since the product is only handled once  
15 while the returning beads may be handled multiple times. A further pulsing gas  
flow, 625, is provided to pulse the beads upwards off the sieves during the  
sieving process. This prevents blinding of the sieve by oversize material and  
replaces the vibration normally provided for sieving which is difficult to implement  
in a non-contaminating system. This gas flow also removes dust particles, which  
20 are blown overhead into a dust collector, 626. This dust is undesirable in the  
product and is likely to contain contaminants from the reactor and from the  
sieving process.

Fig 6b shows one possible variation of this concept where two sieves 631, 632,  
25 are mounted under each other lengthwise in a cylinder, 633, which is then tilted.  
The beads are fed in pulses through Inlet 630. Large beads leave through exit  
tube, 634, into container 635, medium beads through exit tube, 636, into  
container 637, the undersize through exit tube 638 into container 639. Fig 6c is a  
cross-section which shows that the sieves can be slanted to the center to aid in  
30 the transition to the exit tube. The pulsing gas comes in through inlet, 640, and  
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- 5 leaves through exit 641. In design of this variant it is necessary to provide even flow distribution across the sieves which can be done by providing that most of the pressure drop is across the sieves.

An example using Fig 6a is as follows. The feed and exit tubes were 1/4 in i.d.,  
10 the sieve tube was 1 in i.d. Sieve 610 had 1.2 mm holes on a triangular pattern with 1.5 mm spacing. Sieve 616 has 1mm holes on a triangular pattern with 1.2 mm spacing. The angle of the sieves to the horizontal was 45 degrees. The angle of the feed and exit tubes were 30 degrees. The holes were drilled at a 45-degree angle to the plate so the holes were vertical after installation. The  
15 thickness of the silicon sieves was 1.5 mm. The bead pulse size was 6 gm. The gas pulses of stream 625 were 0.8 sec and 0.8 sec off and two pulses were provided per sieving cycle. The sieve cycle time was 6 seconds for a processing rate of 3.6 kg/hr. 1% was carried overheads as dust, 9% of the beads were oversize, 40% were product size and 50% were undersize. All the tubes were  
20 high purity quartz and selected to be low in boron, phosphorus, aluminum, iron and other metals. The sieves were made from high purity undoped silicon wafers which are lower in metals than the high purity quartz and were laser drilled then etched to remove contaminants and surface cracks and to round the edges of the holes.

25

In summary this new machine provides several new techniques which in combination are able to make low cost, shiny, round and high purity silicon granules, using a low cost reactor with low operating costs which overcomes the previous operating problems of contamination, heating, agglomeration and

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- 5 granule size control, is safe and easy to operate, maximizes silicon yield from feedstock and minimizes external support equipment.

- The most important new techniques are; separating the heating of the silicon feedstock gases from the non silicon containing gases and heating the latter to a temperature above the reactor temperature; heating the granules in a heater section and using the pulsing of the gas flow to move the beads into and out of a reactor section; cooling only the localized area around the silicon feedstock entry and minimizing said entries; providing non contaminating sieving and grinding techniques for online removal of large product granules and online or offline grinding of seed granules; a feedstock recovery subsystem which can recycle the byproducts to extinction and providing multiple heater/reactor stages in one vessel.

- Separately heating the silicon feedstock gases means that the diluents may be heated to a much higher temperature however it may be beneficial to introduce small amounts of diluents into the silicon feedstock gases at times and it is certainly required to provide a purge flow when the feedstock gases are not flowing. Heating the granules in a heater section and using the pulsing of the gas flow to move the beads into and out of a reactor section allows the beads to be heated to a temperature higher than the reactor temperature with reduced risk of wall deposit formation then returned to the reactor without contamination and can be done using any heating technique and in conjunction with any other reactor heating technique. The pulsing of the beads back and forth also breaks up agglomerations of beads and prevents channeling inside the reactor so it is possible to provide pulsing for the purposes of agglomeration breakup and use

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5 another heating technique although the method of using the pulsing of the beads  
for both purposes is believed to be the best approach. Cooling only the localized  
area around the silicon feedstock entry and minimizing said entries provides a  
method of preventing silicon deposition in and around the immediate vicinity of  
the nozzle which can ultimately plug the nozzle at a minimum parasitic heat loss  
10 from the cooling. Other approaches are also feasible such as using a lower  
temperature for the silicon containing gases but this imposes a higher heat loss,  
it is also possible to use more nozzles but this has a similar effect. Providing  
non-contaminating sieving and grinding techniques for online removal of large  
product granules and online or offline grinding of seed granules provides a way  
15 to obtain high purity product with one or more narrow size distributions and to  
maintain the granule population in balance by providing seed. The approach  
shown can be partially implemented with some benefits or in different ways. For  
example the beads could be kept hotter which would reduce the heat required to  
reheat the beads returned to the reactor but at the risk of agglomeration and  
20 increased handling problems. The beads could be cooled and reheated using  
heat exchangers to conserve heat at the cost of additional complexity. A  
feedstock recovery subsystem, for trichlorosilane or tribromosilane, which can  
recycle the byproducts to extinction, provides a method for improving silicon  
feedstock utilization and providing a plug-compatible fluid bed reactor system to  
25 replace rod reactors without changing the feedstock production facilities. The  
method shown can be modified to produce more silicon per reactor pass at the  
expense of greater by product production or vice versa and byproducts such as  
dichlorosilane and silicon tetrachloride could be removed in a pure form for sale.  
Providing multiple heater/reactor stages in one vessel gives the opportunity to  
30 add additional reactants such as silane or hydrogen and to obtain larger

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5

### Brief Description of the Drawings

Figure 1a shows the basic way in which the inventions may be combined in a machine for the production of granular silicon.

10 Figure 1b shows ~~how~~ a plan view of multiple tubes and heaters may be used in the heating section of a larger reactor.

Figure 1c shows a cross section along line A-A of Fig 1b.

Figure 2 shows a more detailed schematic of a preferred method to design a silane fluid bed reactor using dual stage injection of silane.

15 Figure 3a shows a more detailed schematic of a preferred method to heat a trichlorosilane fluid bed reactor using a second stage with injection of hot hydrogen gas and TCS and DCS recovery.

Figure 3b is a schematic diagram illustrating one way in which the concepts of the invention for recovery of TCS and DCS can be combined into a complete  
20 reactor system.

Figure 4a is ~~a~~ shows a longitudinal cross section, detailed drawing of a water-cooled nozzle.

Figure 4b, an expanded detail of the water flow in Fig 4a.

Figure 4c is an end view of a water-cooled nozzle shown in Fig 4a.

25 Figure 4bd shows the details of the fabrication of ~~the nozzle at the ball joint of the~~ water cooled nozzle shown in Fig 4a.

Figure 4e shows the cross section at line B-B of Fig 4d.

Figure 4f shows the details of the fabrication of the nozzle tip and reactor connection of the water cooled nozzle shown in Fig 4a.

30 Figure 4g shows the cross section at line C-C of Fig 4f.

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5 Figure 5 shows a layout of the silicon containing gas heater using heat transfer fluid and alternates of internal and external heating of the fluid.

Figure 6a shows a schematic of the bead removal and sieving system

Figure 6b shows an alternative design of the sieving system.

Figure 6c shows a cross section at line A-A of Fig 6b.

10

### Detailed Description of the Preferred Embodiments

Detailed descriptions of the preferred embodiment are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details disclosed herein are not to be  
 15 interpreted as limiting, but rather as a basis for the claims and as a representative basis for teaching one skilled in the art to employ the present invention in virtually any appropriately detailed system, structure or manner.

In order to produce high purity silicon suitable for use in semiconductor or photo voltaic applications it is necessary to form and purify a liquid or gaseous silicon  
 20 containing material then decompose that material back to solid silicon.

Processes to do this have been patented using materials that contain silicon and hydrogen and/or a halogen such as chlorine, bromine or iodine. Such materials include silane, trichlorosilane, dichlorosilane, silicon tetrachloride, tribromosilane etc. It is also common to include a diluent, which may partake in the reaction  
 25 such as hydrogen or be inert such as argon. It is most desirable to recover the material in a convenient pellet or granular form and to have a low cost energy efficient conversion process and to convert as much of the feedstock as possible to usable product. Many patents have identified fluid beds as the appropriate technology to accomplish these aims. Implementation of the fluid bed technology  
 30 has proved difficult and one of the most difficult problems has been providing

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5 sufficient heat at the inlet of the reactor. The heating problem has led to compromises in other areas notably purity and feedstock conversion.

Lack of heat when using silane leads to hydrogen contamination of the product and a dusty product that is not very usable although most of the silane is  
 10 converted. Lack of heat when using trichlorosilane, or other halogen containing feedstocks, leads to poor feedstock conversion. Attempts to increase the feedstock conversion require higher temperatures and lead to contamination from high temperature materials of construction such as graphite or silicon carbide, operating with low feedstock conversion leads to increased cost in  
 15 feedstock production and byproduct disposal or use of more expensive production methods which use higher pressures and temperatures to recycle the byproducts.

Another major problem has been sintering of the granules either at the reactor  
 20 entry or in the body of the bed of particles. Methods of dealing with this problem have been cooling the beads at the entry, using low concentrations of the silicon depositing gas and operating with very vigorous fluidization. Cooling the beads at the entry exacerbates the inlet-heating problem discussed above as does operating with vigorous fluidization. Using low concentrations of the silicon  
 25 depositing gas leads to the uses of large amounts of inerts and the consequent problems of the higher capital and operating cost required to recycle, heat and purify the inerts, which must be maintained exceptionally pure.

A further related problem has been controlling the particle size of the granules in  
 30 the reactor. It is desired to produce beads that are large and of a narrow size  
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- 5 distribution but the reactor fluidizes better with a wide size range and it is desired to minimize contamination in the production of seed. Previous methods of dealing have some or all of the following techniques; particle separation and grinding of seed particles and reintroduction of the seed to the reactor and have done them either internally or externally to the reactor. The problem with
- 10 external techniques has been the contamination and difficulty of control since there is a long lag time (1-2 days) between introduction of small seed particles and their growth to product size. Internal techniques have suffered from the difficulty of separating large granules out and of generating sufficient seed.
- 15 This proposed machine for production of granular silicon incorporates several novel features into its design in order to overcome the above problems without the compromises inherent in the prior technology. The main novel features are; separating the heating of the silicon feedstock gases from the non silicon containing gases and heating the latter to a temperature above the reactor
- 20 temperature; heating the granules in a heater section and using the pulsing of the gas flow to move the beads into and out of a reactor section; cooling only the localized area around the silicon feedstock entry and minimizing said entries; providing non-contaminating sieving and grinding techniques for online removal of large product granules and online or offline grinding of seed granules; a
- 25 feedstock recovery subsystem which can recycle the byproducts to extinction and providing multiple heater/reactor stages in one vessel.

Additional novel features are; heat recovery from granules by direct contact with non silicon containing gases; external flow control of each injection point; heating

30 of the silicon containing gases by a liquid or vapor whose temperature is not high

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5 enough to cause decomposition of the gases, measuring reactor weight and pulsing force continuously and using one or more high efficiency cyclones to removes small diameter dust.

Additional benefits of the design are that separating the heater and reactor  
10 section enables the use of cheap resistance heaters and of different diameters for the two sections, the pulsing action itself polishes the granules, recirculation and reinjection into the reactor of the undersize granules provides new seed particles.

15 In accordance with the present invention, Figure 1a shows a basic version of the invention incorporating several of the novel features in an integrated design that is suitable for production of granular silicon from any silicon containing gas( e.g. silane, dichlorosilane, tribromosilane or trichlorosilane). The recycle of solids is done using a pulsing technique where most of the hot granules in the heater  
20 zone are pushed up into the entry of the reactor by a pulse of gas into the bottom of the heater, Stream 5. At the end of the pulse, colder solids fall down by gravity into the heater for heating and recycle upwards during the next pulse. The pulsing of the beads and gas also provides additional agitation of the bed compared to the agitation provided by the equivalent continuous flow. Such  
25 agitation is particularly useful for silane-based systems, which are primarily limited by the related operational problems of agglomeration and plugging and have been limited to low silane concentrations in the feedstock. Thus the additional heat and agitation provided by pulsing can be used to increase the silicon feedstock flow, stream 1, and thus increase the silicon production, Stream  
30 15 . In Fig1a, stream 1 is shown as broken into two streams, each of which have

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5 their own pulsing devices and inlet coolers, 8a and 8b, which are cooled by inlet  
water flows 9a and 9b and drained by outlet water flows 10a and 10b.

Additional streams typically provided for use in purging lines, initial fluidization,  
 wall deposit etching and shutdown are not shown but are required as is usual for  
 such reactors. Such streams include argon and/or nitrogen for purging and  
 10 fluidization during startup and shutdown and an etching gas such as chlorine or  
 hydrogen chloride for wall deposit etching at the end of the run prior to shutdown.  
 The reactor is supported on a weigh cell or cells, 17, which can provide  
 continuous information on the weight of the reactor and bed and the force of the  
 pulses. Since the pulses are regular and at a known frequency this information  
 15 can be separated from the longer term weight changes by standard frequency  
 analysis techniques. In order to provide accurate information the lines  
 connecting to the reactor must be flexible enough to avoid interfering with the  
 displacement of the weigh cell. Such flexibility is also required to prevent damage  
 to the quartz reactor and allow for differential thermal expansion. This flexibility  
 20 requirement is one reason for the use of the water-cooled ball joint connections  
 with elastomeric O-rings for the nozzle connections, which are shown in Fig 4a-g.

&b. An example of silicon deposition using the design similar to that shown in  
Figure 1a but with three silane inlets, three pulsing devices and three inlet  
coolers, three water inlets, and water outlets instead of the two inlets shown in  
 25 Fig1a is as follows:

A quartz vessel consisting of a bead and gas heater zone of 90 cm length and 5  
 cm in diameter and an insulated reaction zone of 600 cm length and 10 cm  
 diameter was loaded with a 240 cm bed of 850 micron average diameter silicon  
 beads. The three silane inlets for stream 1 were located 100 cm above the  
 30 bottom of the vessel. The reactor, effluent piping and cyclone are well insulated.

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5 The reactor was brought up to 750-800°C using argon as a heating and fluidizing gas through stream, 5, with a small purge stream flow through stream 1. Most of the argon was recycled through stream 5 with some being vented to the effluent gas stream, 4. The hydrogen preheater and the bead /gas heater were set at 900°C, the SCG vapor temperature heater was set at 350°C. The upper wall  
10 heaters were set at 850°C. The pulsing of the argon flow on streams 1, 2 and 5 was started at 0.25 cycle per second in phase. A small cooling water flow of 20 ml/min for each cooling water streams 9a,b&c, 9c not shown in Fig 1a, was started to the silane inlet cooling devices 8a, 8b, 8c, 8c not shown in Fig 1a (25 ml-ee) to provide thermal isolation of the inlet from the reactor temperature. The  
15 inlet water temperature was 35°C and the outlet temperature of the exit cooling water streams, 10 a,b&c, 10c not shown in Fig 1a, was 57°C for a parasitic heat loss of 90 watts. A small flow, 1SLM, of argon was started through stream 62 to the bead cooler, 12, removal tube and a flow of 1 SLM of argon was started to the granule recycle line 16 and silicon sieve, 14, through stream 3. A small flow  
20 of water (100 ml/min) was started to the bead cooler, 12, through stream 11 and exited via stream 13. Then high purity, (less than 2 ppmwt carbon oxides and less than 2ppmw methane) hydrogen was bled into all ~~three~~ four streams 1,2,3&5 to displace the argon with the recycle, 5, temporarily partially closed and effluent gas stream 4 opened more. Once the reactor was at temperature and operating  
25 on hydrogen ~~the hydrogen recovery unit, was started to recover using hydrogen,~~ the temperature of the vapor in the silane heater for stream 1 was controlled at 350°C and silane was slowly introduced. Pulsing continued at 0.25 cycles per second. Simultaneously the temperature of the hydrogen/bead heater at the bottom of the reactor was increased to design conditions of 1000°C for the heater  
30 temperature. At stable operating conditions the silane flow, 1, and the recycle  
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5 kW on average. Power to the hydrogen preheater was 5kW initially decreasing to

5 hydrogen flow, 5, varied between 30-300 SLM to provide the pulsing and were in phase with each other. The individual silane flows ~~4a, b & c~~ each varied between 10-100 SLM in phase. Average bed temperature was 860°C at the bottom, dropping to 840°C at the top of the bed and 685 C at the top of the reactor. Recycle gas from the cyclone was at 410°C and from the hydrogen recovery unit  
10 was 100 °C. The bed was observed to be slugging vigorously at the pulsing cycle of 0.25 cycle/sec and some dust was carried over into the cyclone but pressure drop was stable during the run.

Beads were removed by adjusting the hydrogen flow and pulsing cycle of stream  
15 2. As a pulse of beads left the bead cooler, 12, and went into the silicon sieve, 14, beads from the reactor fell into the bead cooler, 12. The beads going in to the silicon sieve, 14, spread out and either fell through the sieve or were retained and exited as the product stream 15. The beads falling through the sieve were moved by the pulsing of stream 3 back into the reactor via the granule return line  
20 16. The pulsing of stream 3 also assisted in preventing blinding of the sieve, 14. Initially the majority of the beads were smaller than the sieve opening of 1.2 mm and so were recycled. At stable operation the bead removal rate of stream 15 was 13.5 Kg/hr and the bead exit temperature was 80 C. As the bead removal rate was increased the flow of hydrogen through stream 2 was increased and the  
25 flow through the hydrogen preheater was decreased while maintaining the total flow of 30-300 SLM. The flow of stream 3 varied between 10-100 SLM. Thin wall deposits were formed but could be etched off easily at the end of the run. After the run the mass balance showed the deposited silicon was about 95% of the theoretical yield and no major agglomerates were seen. Power to the  
30 hydrogen/bead heater was 3 kW on average. Power to the silane heater was 3

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5 temperature was set at 350 °C. The lower wall heaters were set at 950 °C and the upper wall heaters were set at 850 °C. The pulsing of the argon flow on streams 1, 2 and 5 was started at 0.25 cycle per second in phase. A small cooling water flow of 420 ml/min each was started through cooling water inlet lines, 9a,b&c, 9c not shown in Fig 1a, and 19 a,b&c, 19c not shown in Fig 1a to the silane inlet cooling devices 8a, 8b, 8c, 8c not shown in Fig 1a and 18a,b &c, 189c not shown in Fig 1a (25 ml ea) to provide thermal isolation of the inlet from the reactor temperature. The inlet water temperature was 35 °C and the outlet temperature was 57 °C at the cooling water exit lines, 10 a,b&c, 10c not shown in Fig 1a and 20 a,b&c, 20c not shown in Fig 1a for a total parasitic heat loss of 180 watts. Other conditions and start up procedures were done as for the example above. At stable operating conditions the silane flow, 1, varied between 60-600 SLM and the recycle hydrogen flow, 5, varied between 30-300 SLM to provide the pulsing and were in phase with each other. The individual silane flows 1a, b, c, d, e & f each varied between 10-100 SLM in phase. Average bed temperature was 860 C at the bottom, dropping to 840 °C at the top of the bed and 665 °C at the top of the reactor. Recycle gas from the cyclone was at 400 °C and from the hydrogen recovery unit was 100 °C. The bed was observed to be slugging vigorously at the pulsing cycle of 0.25 cycle/sec and some dust was carried over into the cyclone but pressure drop was stable during the run.

25

Beads were removed as in the example above. The flow of stream 3 varied between 20-200 SLM. The wall deposits that were formed were thicker than in the first example but still could be etched off easily at the end of the run. After the run the mass balance showed the deposited silicon was about 95% of the theoretical yield and no major agglomerates were seen. Power to the

30

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5 advisable. Instead the residual hydrogen must be extracted from the effluent and  
recycled through an external hydrogen recovery system and some additional  
hydrogen is required. In this reactor the lower stage operates at lower hydrogen  
to TCS ratio and at a lower temperature so the thermal decomposition reaction is  
more important. In the upper stage the hydrogen to TCS ratio and the  
10 temperature is increased thus using the hydrogen reduction reaction to obtain  
additional yield of silicon. Since the TCS is fed as a liquid some changes were  
made to the metering equipment and to the preheater which now also was to be  
used as a vaporizer. The heat requirement were a little less than for silane  
because of the lower TCS flow. In order to maintain the pulsing, spray nozzles  
15 and liquid solenoid valves were placed directly on the inlet to the vaporizer.

A small cooling water flow of 60 ml/min was started to the silane inlet cooling  
devices 8a, 8b, 8c, 8c not shown in Fig 3a, (20 ml ea) and 90 ml/min to 18a, b  
&c, 18c not shown in Fig 3a, (30 ml ea) to provide thermal isolation of the inlet  
20 from the reactor temperature. The inlet water temperature was 35°C and the  
outlet temperature was 57°C for 8a, b &c and 65°C for 18,a,b &c for a parasitic  
heat loss of 270 watts. Other conditions and start up procedures were done as  
for the example above. After startup on hydrogen was achieved with the bed at  
850°C the temperatures of the hydrogen/bead heater at the bottom of the reactor  
25 was increased to 1000°C, the lower wall heaters were increased to 1050°C and  
the upper heaters to 1150°C.

At stable operating conditions the trichlorosilane/dichlorosilane (98% TCS) flow in  
stream 1 was 12-120 SLM (4-40SLM per injector) and the temperature was  
30 350°C, the ultra pure (less than 0.2 ppmwt carbon oxides and 0.2 ppmwt  
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methane) hydrogen flows in stream 5 and 17 were varied between 30-300 SLM and the hydrogen flow to the bead cooler was 2-20 SLM. Bed temperature was 860°C at the trichlorosilane inlet, increasing to 1100°C at the top of the bed and 1050°C at the top of the reactor. Beads were removed as in the example above. The flow of stream 3 varied between 2-20 SLM. ~~The~~ Silicon tetrachloride vapor, 21, was added ~~at~~ to the top of the reactor, ~~stream 21, the~~ at a temperature is ~~of~~ 100 °C and the flow is ~~of~~ 75 SLM. ~~Recycle gas from~~ The gas exit temperature from the cyclone was at 900°C and from the hydrogen recovery unit was 20°C. The wall deposits that were formed were thicker in the wall heater zones but still could be etched off easily at the end of the run. After the run the mass balance showed the deposited silicon was about 95% of the theoretical yield and no major agglomerates were seen. Power to the hydrogen/bead heater was 4 kW on average. Power to the trichlorosilane vaporizer/heater was 2.5 kW on average. Power to the hydrogen preheater was 5kW , to the hydrogen superheater was 10 kW . Power to the lower wall heaters was 3kW on average. Power to the upper wall heaters varied between 5 and 7 kW depending on the amount of cold undersize granules recycled to the reactor. The silicon production was 1 kg/hr, which is about 25% of the silicon in the TCS. Power required was about 30 kW/kg. Energy requirements are based on a trichlorosilane liquid feed. It should be noted that in a dedicated TCS reactor the upper injectors for superheated hydrogen only need to be cooled at the joint not at the reactor penetration, which would save a small amount of heat (about 150 watts). The energy required to vaporize and heat the silicon tetrachloride is not included because this is part of the recovery operation. Ultra pure hydrogen is required because of the greater hydrogen to silicon ratio in this reactor compared to a silane reactor. The specific level of purity required for the hydrogen diluent

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5 may be calculated by mass balance based on the silicon specification and the assumption that all carbon entering the reactor leaves in the silicon product.

The benefit of injecting the silicon tetrachloride at the top of the reactor is to  
 10 move the equilibrium conditions so as to recover additional feedstock. The schematic of this sub-system is shown in Fig 3b. The silicon feedstock stream, 301, is mixed with the recycle stream 317 to form reactor feed stream, 310, ~~(corresponding to stream 1 in Fig 3a)~~ which is heated in the TCS heater, 322, to a temperature below its thermal decomposition temperature. The hydrogen  
 15 feedstock stream, 302, is mixed with the recycle stream 313 to form reactor feed stream, 320, ~~(corresponding to stream 5 in Fig 3a)~~ heated in the hydrogen heater, 323, and then reacts in the reactor, 303. The use of multiple heaters and injection points as done in the preferred embodiment of the reactor does not affect the basic schematic. The silicon product leaves the reactor as Stream  
 20 304 15.

The stream 305 enters the recovery reactor 306 (corresponding to the effluent piping and cyclone of Fig3a) where it is preferably combined with the STC stream 318 ~~(corresponding to stream 21 in Fig 3a)~~ and cools and reacts to reform the desired feedstock. This stream, 307, exits the recovery reactor and enters the  
 25 rapid quencher, 308, where the gases are cooled rapidly to prevent decomposition of the newly reformed feedstock. The stabilized gases, 309, exiting the quench are then cooled further in the gas -liquid separator, 310, to condense most of the silicon containing species and the condensed liquids, 311, are separated from the uncondensed gases, 310, which are primarily hydrogen  
 30 and hydrogen halides and are further treated in a gas separator, 312, to provide

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5 a stream, 313, that is primarily hydrogen and a stream, 314, that contains most of the hydrogen halide. This gas separator can be a cryogenic device, an absorption or adsorption device, a membrane device or any combination thereof. The liquid stream, 315, is then processed in a liquid separator, 316, into a stream, 317, which is primarily silicon hydrogen halides and a stream, 318, which is

10 substantially free of silicon hydrogen halides. All or part of stream 318 may be recycled to the recovery reactor, 306, through STC heater, 324 as stream 21 or sent directly to the decomposition reactor, 303, through STC heater 325 as in the prior art. As discussed earlier returning the STC stream directly to the decomposition reactor has significant disadvantages which why it is not the

15 preferred option. ~~Such a~~ The separator, 316, will typically be a distillation column but any techniques are suitable which will provide good separation. The required degree of separation is determined by economics but typically the purity of each stream would be about 98-99%. The benefit of such a scheme is that the effluent from the system is only stream 314 which contains mostly hydrogen chloride

20 which can be directly recycled to react with silicon to make more TCS at >90% yield. There is no recycle of pure silicon containing materials back to the low purity TCS manufacturing unit and there is no waste STC stream that must be converted to low value silica. Thus while the preferred reactor subsystem is more expensive to build and operate than one without feedstock recovery and

25 thus designed with lower hydrogen flows and higher TCS flows the overall system is more economic because of reduction in costs of the remaining systems. A further reason for this preferred design is that it is ~~plug-in~~ very compatible with can easily be substituted for the standard existing rod reactors because they also recycle the STC to extinction. Use of apparently cheaper

30 reactors which do not fully convert the silicon content in the TCS as substitutes

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5 for existing rod reactors would mean either a reduction in silicon output or the need for expansion and modification of the TCS production and purification facilities.

A key feature of the machine is the localized cooling of the silicon containing gas injector nozzles. Figs 4a-g shows one way this may be implemented. Fig 4a is a cross section of the nozzle assembly. The silicon containing gas at about 350°C, stream 401, comes in through the ball joint, 402, which is sealed by an elastomeric o-ring, 403, positioned in an o-ring groove, 404, and which is cooled by water flowing through a micro-channel, 405, directly under the o-ring groove .

15 It proceeds through the inside of the inner quartz tube 406, which tapers down as it enters the reactor, 407. The tip of the nozzle, 416, is cooled by water flowing through the circumferential micro-channel, 408 which is cut into the outer wall of the inner tube, 406 and sealed against the inner wall of the outer tube, 409.

Water flows from the water inlet 410, to the ball joint micro-channel, 405, via a micro-channel, 411, which is cut into the outside of the inner tube 403 and then goes to the tip micro-channel, 408, via a micro-channel, 412 on the other side of the outside of the inner tube 406. This water is returned to the outlet, 414, via a return micro-channel 413. There several features which are important. The machining of the circumferential micro-channels must ensure that the water flows

25 evenly on both sides. The water in the circumferential micro-channels must flow fast enough, 10-100 cm/s, to obtain good heat transfer at the tip. The supply and return micro-channels must not cross each other. In Fig 4a way the incoming cold water goes first to the ball joint via 411 then to the tip via 412 and is returned via 413 which is separated from 411 by an uncut section of quartz between the

30 inlet and outlet water tubes, 410 and 414. Fig 4b is an enlarged drawing of the

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5 section between the inlet and outlet water tubes, 410 and 414 to better show the  
water flowpath. Fig 4c shows an end view of the nozzle and illustrates how the  
inlet tube 410 may be bent away from exit tube 414 to provide access for  
connections. This design provides higher flow rates than if the flow was divided  
and avoids the problems of starving one section through flow maldistribution.

10 It is of course possible to have more than one circumferential micro-channel  
providing good engineering practice is followed in design and fabrication to  
prevent flow maldistribution. Figs 4d-g shows some details of the nozzle tip and  
ball joint. In Fig 4g  $\mp$  the nozzle tip micro-channel, 408, is shown as a micro-  
channel that is 3mm wide and 0.2 mm deep with its far end 1 mm from the end of  
15 the nozzle. The nozzle tip 416 is rounded which reduces chipping damage and  
removes a hot spot on the end of the nozzle where deposition might occur. The  
nozzle is supported by 4 quartz nibs, 415, which provide additional strength  
without contributing much to the heat transmitted back to the nozzle from the  
reactor wall. In the Fig 4f which is a cross section A-A, the four quartz nibs, 415,  
20 are shown to have little area in contact with the nozzle and the circumferential  
water channel 408 is shown as an annular space. In Fig 4e which is the cross  
section B-B the supply, 412, and return, 413, micro-channels are shown as  
sectors produced by grinding flats on the outer wall of the inner tube 406. It is  
of course possible to grind multiple flats or to grind other shapes providing that  
25 the strength of the inner tube is adequate after grinding and that the hydraulic  
diameter of the micro-channel is large enough to allow the required cooling water  
flow at the available pressure drop.  $\mp$  In the Fig 4d the ball joint is shown as a  
standard 18/7 ball o-ring joint with a diameter of 18 mm at the widest end of the  
o-ring groove micro-channel, 404, a tube outside diameter of 9.5 mm and a  
30 nominal internal diameter of 7 mm, sealed to the inside of this is a 5-7.25 quartz  
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5 tube which has been OD ground to fit tightly. The tight fit provides the water seal between the entrance and return water lines. Circumferential micro-channels are cut in the outside of this inner tube to provide the cooling at the ball joint and tip and flats are ground to provide the water connections. The inner and outer tubes are assembled, welded, annealed, ground to obtain the final shape then acid

10 treated to improve the surface finish and strength. The water connections shown are standard 12/2 ball o-ring joint with a diameter of 12 mm at the widest end of the o-ring groove, a tube outside diameter of 6 mm and a nominal internal diameter of 2 mm. The relatively thick wall, 2mm, is beneficial in preventing accidental breakage. The problem of accidental breakage is a major design

15 issue for these quartz injectors because of the safety issues involved in handling pyrophoric materials. Simply making the injectors very large with thick walls increases the heat transmission back from the reactor and even such designs are prone to breakage if sufficient force is applied particularly if there is a lever action involved such as is the case with the injectors since they must penetrate

20 the insulation. Thus it is important to prevent movement of the nozzle so the rigid insulation used has recesses cut in the top to support the water connections. It is also important to prevent force being applied to the end of the nozzle by the connections so they must be very flexible. The water connections can be small diameter 1/8 inch tubing and coiled helically to provide flexibility.

25 The silicon containing gas connections typically need to be 1/4" tubing, stainless steel and insulated. However the pressure is low so thin wall corrugated tubing can be used and a similar helical coil may be employed. It is also possible to put short , 1 ft, lengths of smaller 1/8in or 3/16 in dia. tubing without increasing the pressure drop too much. The insulation must not restrict the movement of the

30 tubing needed to accommodate differential thermal expansion during the various

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5 reactor operations. Selection of the O-ring material is also important as this provides a safety and contamination barrier for the reactor. The o-rings are usually selected from an elastomeric fluorocarbon material such as Viton or Kalrez because of temperature considerations. The permeability of such material to contaminants such as oxygen, carbon dioxide and water vapor in the  
10 atmosphere varies with material composition and temperature. The materials can also slowly deteriorate giving off contaminants. The most critical consideration is control of the o-ring temperature, which should be maintained in the 25-150°C range and preferably around 50°C. It is of course possible to use multiple o-rings for additional protection at some increased expense but all o-rings must have  
15 their temperature maintained in the desired temperature range.

Fig 5 shows a layout of a preheater for a silicon containing gas. It consists of a gastight vessel, 501, which contains three helical coils, 502, 503 & 504, of tubing each of the same length coiled concentrically in the top half and one or more  
20 electrical elements, 505, in the bottom half. The vessel is filled with high temperature heat transfer fluid, 506, so as to cover the heating element/s, 5, during operation. A temperature indicator controller or TIC, 507, is provided to control the temperature of the fluid below the silicon containing gas decomposition temperature, 300-400°C. Each coil has separate inlets, 508, 509,  
25 510 and outlets, 511, 512, 513. The lid, 514, is flanged to the top of the vessel and is removable for access to the coils. A connection, 517, for a pressure gage and pressure relief valve is provided. The penetrations of the coils through the lid are gas tight, typically welded. During operation the silicon containing gas comes in through the separate inlets and leaves without mixing through the outlets. The  
30 coils are free to expand and thus exert no force on the connections through the lid which reduces the risk of leaks commonly found at the tube to tubeplate connection of shell and tube heat exchangers. The heat to the coils is supplied

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5 by condensing heat transfer fluid vapor, which is produced by boiling the fluid with the electric heating element, 505. Alternatively the liquid may be removed through liquid outlet, 515, and vaporized in an external vaporizer, not shown as dotted lines, then returned through the fluid inlet, 516, or the liquid may be removed then heated but not vaporized and returned through, 516. In this latter

10 case it may be necessary to provide baffles and a higher mass flow rate to provide adequate heat transfer. There are many other variants, such as providing more than three coils, using U-shaped tubes or pancake coils which one knowledgeable in the art can design. The coils may be straight tubing, corrugated, twisted or finned.

15 In an example of operation of this device the gas tight vessel, 501, was 10 inches in diameter and 15 inches tall and fabricated from 304L stainless steel. It was insulated on the top, bottom and sides with a 2" thick layer of Microtherm G pressed silica insulation, 518. The coils, 502, 503 & 504 were each 10 ft long and made from 1/4-inch 304L S. S. tubing. The coil diameters were approximately 6

20 inches, 7 inches and eight inches. The electrical heater was a 4" diameter flange mounted heater of 4 kW with multiple Incoloy sheathed elements. The heat transfer fluid was filled to a depth of 8 inches. The fluid used was Dowtherm A. Temperature of operation was controlled at 360 C (680 F) using the temperature indicator controller. Pressure in the vessel was 75 psig. The three coils each

25 heated an average of 67 SLM of silane each from 20C to 330 C. Actual flow of silane per tube pulsed from 10-100 SLM.

Fig 6a shows a schematic representation of the non-contaminating sieving device. The hot beads, stream 601, fall into a cooler, 602, where a gas stream

30 603 may cool them, which then goes back up into the reactor thus recovering some heat from the beads. In addition the beads may be cooled by a water

5 jacket, 605, with inlet an outlet streams, 605a & 605b. A gas stream 606 is pulsed into tube, 607, which also may be cooled by a water jacket, 608, if desired. The pulsing gas stream pushes a fixed amount of beads out of the cooler, 602, into the siever tube 609. The beads fall onto the first sieve, 610, and the beads smaller than the sieve pass through while the larger beads are retained and exit

10 through stream, 611. These beads may be pulsed using the gas stream 612 through a tube 613 into a container 614. It is advantageous to use a bead detection device, 615, to adjust the bead flow into the container 614 so as to maintain the exit tube, 611, full or nearly full of large beads. This reduces the chance of smaller beads exiting with the large beads and provides a

15 measurement of the flow of large beads since the pulsing flow of the gas stream 612 may be correlated with the bead flow. The sieving process may be repeated as shown with a smaller size sieve, 616, using tubes 617 and 619, gas flow 618 and container 620. The residual undersize beads then fall to the bottom, 621, where they can be removed via tube 623 and gas stream 622 to a container 624.

20 This container can be used to replenish the reactor in a variety of ways apparent to one skilled in the art including pneumatic transport and physically moving the container to a bead feeding port. Such beads may also be reheated. All material with which the beads come into contact must be noncontaminating. Such materials include electronic grade silicon and high purity silicon oxide. The

25 degree of contamination that may be permitted is higher for the product beads than for the return beads since the product is only handled once while the returning beads may be handled multiple times. A further pulsing gas flow, 625, is provided to pulse the beads upwards off the sieves during the sieving process. This prevents blinding of the sieve by oversize material and replaces the

30 vibration normally provided for sieving which is difficult to implement in a non-

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5     contaminating system. This gas flow also removes dust particles, which are  
       blown overhead into a dust collector, 626. This dust is undesirable in the product  
       and is likely to contain contaminants from the reactor and from the sieving  
       process.

10    Fig 6b [[A]] shows one possible variation of this concept where two sieves 631,  
       632, are mounted under each other lengthwise in a cylinder, 633, which is then  
       tilted. The beads are fed in pulses through inlet 630. Large beads leave through  
       exit tube, 634, into container 635, medium beads through exit tube, 636, into  
       container 637, the undersize through exit tube 638 into container 639. Fig 6c is a  
       The cross-section which shows that the sieves can be slanted to the center to aid  
       in the transition to the exit tube. The pulsing gas comes in through inlet, 40, and  
       leaves through exit 41. In design of this variant it is necessary to provide even  
       flow distribution across the sieves which can be done by providing that most of  
       the pressure drop is across the sieves.

20    An example using Fig 6a is as follows. The feed and exit tubes were 1/4 in i.d.,  
       the sieve tube was 1in i.d. Sieve 610 had 1.2 mm holes on a triangular pattern  
       with 1.5 mm spacing. Sieve 616 has 1mm holes on a triangular pattern with 1.2  
       mm spacing. The angle of the sieves to the horizontal was 45 degrees. The  
       angle of the feed and exit tubes were 30 degrees. The holes were drilled at a 45-  
       degree angle to the plate so the holes were vertical after installation. The  
       thickness of the silicon sieves was 1.5 mm. The bead pulse size was 6gm. The  
       gas pulses of stream 625 were 0.8 sec and 0.8 sec off and two pulses were  
       provided per sieving cycle. The sieve cycle time was 6 seconds for a processing  
       rate of 3.6 kg/hr. 1% was carried overheads as dust, 9% of the beads were  
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5    oversize, 40% were product size and 50% were undersize. All the tubes were  
high purity quartz and selected to be low in boron, phosphorus, aluminum, iron  
and other metals. The sieves were made from high purity undoped silicon wafers  
which are lower in metals than the high purity quartz and were laser drilled then  
etched to remove contaminants and surface cracks and to round the edges of the  
10   holes.

In summary this new machine provides several new techniques which in  
combination are able to make low cost, shiny, round and high purity silicon  
granules, using a low cost reactor with low operating costs which overcomes the  
15   previous operating problems of contamination, heating, agglomeration and  
granule size control, is safe and easy to operate, maximizes silicon yield from  
feedstock and minimizes external support equipment.

The most important new techniques are; separating the heating of the silicon  
20   feedstock gases from the non silicon containing gases and heating the latter to a  
temperature above the reactor temperature; heating the granules in a heater  
section and using the pulsing of the gas flow to move the beads into and out of a  
reactor section; cooling only the localized area around the silicon feedstock entry  
and minimizing said entries; providing non contaminating sieving and grinding  
25   techniques for online removal of large product granules and online or offline  
grinding of seed granules; a feedstock recovery subsystem which can recycle  
the byproducts to extinction and providing multiple heater/reactor stages in one  
vessel.

5 Separately heating the silicon feedstock gases means that the diluents may be heated to a much higher temperature however it may be beneficial to introduce small amounts of diluents into the silicon feedstock gases at times and it is certainly required to provide a purge flow when the feedstock gases are not flowing. Heating the granules in a heater section and using the pulsing of the gas

10 flow to move the beads into and out of a reactor section allows the beads to be heated to a temperature higher than the reactor temperature with reduced risk of wall deposit formation then returned to the reactor without contamination and can be done using any heating technique and in conjunction with any other reactor heating technique. The pulsing of the beads back and forth also breaks up

15 agglomerations of beads and prevents channeling inside the reactor so it is possible to provide pulsing for the purposes of agglomeration breakup and use another heating technique although the method of using the pulsing of the beads for both purposes is believed to be the best approach. Cooling only the localized area around the silicon feedstock entry and minimizing said entries provides a

20 method of preventing silicon deposition in and around the immediate vicinity of the nozzle which can ultimately plug the nozzle at a minimum parasitic heat loss from the cooling. Other approaches are also feasible such as using a lower temperature for the silicon containing gases but this imposes a higher heat loss, it is also possible to use more nozzles but this has a similar effect. Providing

25 non-contaminating sieving and grinding techniques for online removal of large product granules and online or offline grinding of seed granules provides a way to obtain high purity product with one or more narrow size distributions and to maintain the granule population in balance by providing seed. The approach shown can be partially implemented with some benefits or in different ways. For

30 example the beads could be kept hotter which would reduce the heat required to

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- 5 reheat the beads returned to the reactor but at the risk of agglomeration and increased handling problems. The beads could be cooled and reheated using heat exchangers to conserve heat at the cost of additional complexity. A feedstock recovery subsystem, for trichlorosilane or tribromosilane, which can recycle the byproducts to extinction, provides a method for improving silicon
- 10 feedstock utilization and providing a plug-compatible fluid bed reactor system to replace rod reactors without changing the feedstock production facilities. The method shown can be modified to produce more silicon per reactor pass at the expense of greater by product production or vice versa and byproducts such as dichlorosilane and silicon tetrachloride could be removed in a pure form for sale.
- 15 Providing multiple heater/reactor stages in one vessel gives the opportunity to add additional reactants such as silane or hydrogen and to obtain larger throughputs for a given footprint. It also allows production of very large beads in the bottom section and in the case of silane operation at lower hydrogen to silane ratios, which reduces the risk of contamination. It is possible to have as many
- 20 stages as is desired and to adjust the diameter of each section independently.

Additional novel features are; heat recovery from granules by direct contact with non silicon containing gases; external flow control of each injection point; heating

25 of the silicon containing gases by a liquid or vapor whose temperature is not high enough to cause decomposition of the gases, measuring reactor weight and pulsing force continuously and using one or more high efficiency cyclones to removes small diameter dust.